

First-principles study of the stability of free-standing germanene in oxygen

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The O₂ dissociation and O atoms adsorption on free-standing germanene are studied by using first-principles calculations in this letter. Compared with the spontaneous dissociation of oxygen molecule on free-standing silicene in air, germanene is more stable than silicene from kinetic point of view, with overcoming energy barrier of about 0.55 eV. Especially, in contrast with the unique chemical adsorption of O₂-dissociation-induced O atoms on silicene, oxygen molecule can behave a correspondingly stable adsorption on germanene surface. Moreover, single O atom adsorption on germanene is also different to that on silicene, resulting in two opposite migration pathways on germanene surface. Furthermore, once the oxygen molecule dissociates into O atoms on germanene surface, the migration and desorption of O atoms are relatively difficult under room temperature due to the strong Ge-O bonds in the O-adsorbed germanene, in favor of forming germanium oxides. The results provide compelling evidence to show that free-standing germanene is relatively stable in oxygen, which is different to silicene essentially.

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I. INTRODUCTION

Graphene, a single layer material of carbon atoms with two-dimensional (2D) honeycomb structure, has attracted intensive attention from scientific community to industry field for its remarkable properties.¹⁻⁵ Since the discovery of graphene in 2004, other 2D layered materials similar to graphene, such as silicene and germanene, have gained renewed interest because it is important for people to look for 2D materials based on existing silicon or germanium electronic industry. As group-IV element graphene-like 2D sheet, most of the known features of germanene resemble those of silicene. Theoretically, density functional theory (DFT) studies of silicene or germanene have illustrated that silicon or germanium prefers *sp*³ hybridization instead of *sp*², thus, silicene or germanene is energetically favorable as a low-buckled (LB) structure with an amplitude of about 0.44 Å and 0.69 Å.^{6,7} Moreover, the band structures in the LB configurations of silicene and germanene are ambipolar, and their charge carrier can behave like a massless Dirac fermion at the K point because of the π and π^* bands that linearly cross at the Fermi level. It is also found that the electronic and magnetic properties of silicene and germanene nanoribbons show size and geometry dependence.⁸ Furthermore, phonon calculations demonstrate the stability of silicene and germanene in their ground states.^{9,10} In addition, recent studies predict that SOC effect can open a 1.5 meV band gap in silicene as well as 25 meV in germanene,^{7,11} useful to the topological insulators.

Experimentally, using atomic resolved scanning tunneling microscopy (STM), it has been demonstrated that

silicene can be grown on a close-packed silver surface [Ag (111)] or ZrB₂ substrate via direct condensation of a silicon atomic flux onto the single-crystal substrate in ultra-high vacuum conditions.^{12,13} One year later, it is reported once more on an iridium (111) surface.¹⁴ Furthermore, germanane, the fully hydrogenated germanene, has also been fabricated using a wet chemistry method in 2013.¹⁵ However, germanene, which has already been predicted to be stable as freestanding novel monolayer germanium, has remained elusive. It seems to still exist only in the theory. But quite recently, an exciting experiment by Dávila et al¹⁶ shows that, a two-dimensional germanium layer, forming several phases, has been grown *in situ* by dry deposition of germanium onto the Au(111) surface, similarly to the formation of silicene on Ag(111). One of these phases displays a clear honeycomb structure with a very weak corrugation in STM imaging. Additionally, detailed core-level spectroscopy measurements along with advanced density functional theory calculations identify this phase as a $\sqrt{3}\times\sqrt{3}$ reconstructed germanene layer on top of a $\sqrt{7}\times\sqrt{7}$ Au(111) surface. Nevertheless, the resistance to oxidation has not been concerned in their report. To our best knowledge, the resistance to oxidation of a novel material is an essential prerequisite for its future applications.

In our previous work,¹⁷ it shows that free-standing silicene is extremely active in oxygen due to the spontaneous dissociation of O₂ molecule on silicene without overcoming any energy barrier, implying an exothermic process essentially. Moreover, the migration and desorption of O atoms are relatively difficult under room temperature because of the strong Si-O bonds in the O-adsorbed silicene, which is in favor of forming silicon oxides. Therefore, in order to take advantage of the good electronic characters of silicene, some ways to protect the silicene from exposing to oxygen must be found out, like

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Molle's¹⁸ methodology of encapsulated silicene by oxides-covered heterostructures. As mentioned above, it naturally raises a question: Can free-standing germanene be stable in oxygen?

To answer this question and further understand the details of interaction between oxygen molecule and germanene surface, the O_2 dissociation and O atoms adsorption on free-standing germanene are studied by using first-principles calculations in this letter. Our results show that, in comparison to extreme activity of silicene in oxygen, germanene is relatively stable on account of the energy barrier of about 0.55 eV to overcome. Moreover, oxygen molecule can be stably adsorbed on germanene surface, differing in the case of barely chemical adsorption of O atoms on silicene. Furthermore, O atoms adsorbed on germanene are relatively difficult to migrate on or be desorbed from surface, leading to poor mobility of O atoms.

II. METHOD

All calculations are performed by using the VASP (Vienna ab initio simulation package)¹⁹ within the projector augmented-wave (PAW) approach.²⁰ The ground state of the electronic structure is described within density functional theory (DFT) using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional.²¹ The energy cutoff for expansion of wave functions and potentials is 550 eV. The single layer germanene is modeled with a $4 \times 4 \times 1$ supercell containing 32 Ge atoms. All of models are separated with a 15 Å vacuum layer in the z-axis direction. Monkhorst-Pack special k-point method²² is used with a grid of $3 \times 3 \times 2$. The entire systems are relaxed by conjugate gradient method until the force on each atom is less than 0.03 eV/Å. To optimize the O_2 molecule dissociation path, the climbing image nudged elastic band (CINEB) method²³ is employed, which has been proved to be quite effective to calculate the diffusion energy barrier.

III. RESULTS AND DISCUSSIONS

To investigate the stability of germanene in oxygen accurately, the lattice and geometry of the low-buckled germanene unit cell is optimized, as shown in Fig. 1. The lattice constant $a=4.06$ Å and buckling $\Delta=0.69$ Å are obtained. The corresponding DOS shows the semimetallic or zerogap semiconducting character of germanene, in agreement with the previous report.⁷

To simulate the Ge-O ratio dependance of the O_2 molecule adsorption on germanene, one O_2 molecule is put on unit cells with different sizes from $1 \times 1 \times 1$ to $4 \times 4 \times 1$. Results show that for all the unit cell sizes applied, if the interaction between O_2 molecule and germanene is strong enough, O_2 molecule dissociates into

two O atoms that bond tightly with Ge atoms after relaxation, which indicates that the process of dissociation is independent of the size of unit cell. In the following, a $4 \times 4 \times 1$ super cell is used to further investigate the dependence of O_2 dissociation on initial positions and orientations of the O_2 molecule. Different separation distance between O_2 and germanene are tested, which are 0.60, 1.50, 3.00, 4.00 and 6.60 Å, respectively. For each distance, the O_2 molecule is rotated and its initial position is also adjusted.

It is found that, when the distance is 6.60 Å, the optimized adsorption distance decreases to about 6.40 Å and the orientation of oxygen is barely changed. The O-O bond length corresponds to 1.25 Å, slightly longer than that of 1.23 Å in vacuum. The corresponding adsorption energy (defined as the energy difference between the total energy of O-adsorbed germanene and the sum of the total energies of the free isolated O_2 molecule and free-standing germanene) is nearly 0 eV, indicating that the interaction between the O_2 molecule and the germanene is rather weak under this condition. It means a poor physical adsorption.

While the distance are 4.00 Å, 3.00 Å and 1.50 Å, respectively, results show that oxygen molecule has been adsorbed on germanene surface after relaxation. The corresponding O-O bond length, Ge-O bond length and the adsorption distance are about 1.44 Å, 1.94 Å and 1.78 Å, respectively. The adsorption energy corresponds to 1.76 eV. Compared with the poor physical adsorption, it shows that the interaction between oxygen and germanene surface becomes stronger. On the other hand, it also means that the O_2 adsorption is independent of the initial position and orientation of the molecule for the separation of 1.50 Å and 4.00 Å, implying a spontaneous adsorption of oxygen molecule if the interaction is strong enough. Importantly, the O-O bond length of 1.44 Å, the Ge-O bond length of 1.94 Å indicates that the O-O bond is not broken and Ge atoms bond with O atoms, showing a chemical adsorption of oxygen molecule on germanene which is so different to silicene. Especially, the corresponding adsorption energies of 1.76 eV is quite large for simple physical adsorption. Therefore, charge transfer might occur when O_2 molecule is adsorbed on the germanene surface. In order to verify this, the induced charge density defined as

$$\Delta\rho = \rho(Ge_{32}O_2) - \rho(Ge_{32}) - \rho(O_2)$$

is plotted in Fig. 2, where $\rho(Ge_{32}O_2)$ and $\rho(Ge_{32})$ are the charge density of the germanene system with and without O_2 adsorbed on the surface, respectively. $\rho(O_2)$ is the charge density of O_2 molecule. With this definition, isosurfaces of positive values indicate gain charge, while negative values indicate loss charge during the adsorption process. It shows clearly from Fig. 2 that O_2 molecule gains abundant charge when it is adsorbed on the germanene surface, while two Ge atoms bonded with two O atoms loss the charge. It indicates the stronger

interaction and bond strength between Ge and O atoms.

As the separation distance decreases to 0.6 Å, the dissociation of oxygen molecule happens. The oxygen molecule dissociates into two O atoms on different bridge sites of two nearest neighboring Ge atoms. The adsorption energy corresponds to 4.08 eV. The corresponding O-O distance and Ge-O bond length are 3.34 Å and 1.83 Å, respectively, implying that the O-O bond has been broken.

After dissociation, the most stable configuration of the two O atoms is calculated to be locating at two bridge sites. To investigate the detail of O₂ molecule dissociation on germanene surface and obtain the optimized dissociation pathway of O₂, the CINEB method is applied. As the distance decreases from 4.00 to 3.00 then to 1.50 Å, the oxygen molecule is all adsorbed on germanene. Therefore, the optimized adsorption state with the lowest energy corresponding to separation distance of 3.00 Å can be regarded as initial state in CINEB method. The O₂ dissociation state with the two O atoms locating on two bridge sites can be regarded as Final state. The state of two O atoms locating on two top site of germanene is calculated as transition state. To illustrate the spontaneous adsorption of oxygen on germanene, the evolution from the free O₂ molecule to adsorbed oxygen molecule is also considered in our calculations. The optimized dissociation pathway of oxygen molecule is shown in Fig. 3. The spontaneous oxygen molecule adsorption on germanene surface can be seen in Fig. 3(a)-(b), indicating an exothermic process which is similar to the O₂ dissociation on silicene. This may originate from gradually strengthened Ge-O bond, which lowers energy of the system substantially. But from Fig. 3 (b)-(d), the most important dissociation process of oxygen molecule shows that there is a energy barrier of about 0.55 eV to overcome. From the thermodynamic point of view, the O₂ molecule dissociation reaction on germanene is also an exothermic process. Kinetically, in comparison with the spontaneous O₂ dissociation on silicene, the energy barrier of about 0.55 eV indicates that freestanding germanene is more stable than silicene in the presence of O₂ and its dissociation reaction is quite different from that of silicene intrinsically. In this proceeding, Ge-O bond become further strengthened while O-O bond become further weakened, resulting in the Ge-O and O-O bond lengths change from 1.94 Å, 1.44 Å to 1.84 Å, 1.89 Å, as shown in Fig. 3 (c). Sequentially, as a result of durative exothermic process, the dissociation reaction of oxygen molecule comes from transition state into final state, as shown in Fig. 3 (d). The corresponding O-O distance is also changed from 1.89 Å to 3.34 Å. Compared with the 1.23 Å in vacuum, the O-O distance of 3.34 Å shows that the O₂ totally dissociates on germanene. On the other hand, the corresponding adsorption energy of 4.08 eV in final state is lower than that of 5.36 eV on silicene, demonstrating that the silicon oxide is more stable than germanium oxide from another perspective.

Since oxygen molecule can dissociate into two O atoms

on germanene surface, the adsorption and the activity of O₂-dissociation-induced O atoms are necessary to be discussed to further understand the stability of the most favorable adsorption sites. Four typical adsorption sites of the O atom are considered in our calculations which are the bridge site of two nearest-neighboring Ge atoms, the top sites of two different Ge atoms and the center site of Ge₆ ring, marked with 1, 2, 3, and 4 in Fig. 4(a), respectively. Sites 2 and 3 are different due to the buckling of the germanene. The adsorption energy (E_{ad}) is defined as:

$$E_{ad} = -[E(Ge_{32}O) - E(Ge_{32}) - 1/2 \times E(O_2)]$$

where the $E(Ge_{32}O)$ and $E(Ge_{32})$ are the total energy of the germanene supercell model with and without adsorption of one O atom, respectively. $E(O_2)$ is the total energy of O₂ molecular in vacuum. The calculated adsorption energy E_{ad} and adsorption distance D (defined as the distance from the adsorbate to the substrate plane, namely, the difference between the z -axis coordinate of the adsorbate and the average of z -axis coordinate of all surface atoms) for the adsorption of an O atom on different sites of germanene are listed in Table 1.

It is found that the strongest adsorption of one O atom on germanene is locating at the bridge site (site 1) with adsorption energy of 2.14 eV and adsorption distance of 1.59 Å, corresponding to the most favorable dissociation sites of the O₂ molecule, as shown in Fig. 4 (b). The corresponding Ge-O bond length between the O atom and the neighboring Ge atom is about 1.84 Å. Interestingly, it can be seen from Fig. 4 (c) that the O atom adsorbed on top site 2 drops down to but the Ge atom is pulled out of the basin plane of germanene after relaxation, which is quite different from the case of top site 3. It may originate from the slightly longer Ge-Ge bond length and weakened Ge-Ge bond strength, compared with that of silicene.

To examine the activity of the adsorbed O atoms, the diffusion of the O atom on germanene is investigated thoroughly. In order to find the optimized migration pathways, the CINEB method is also applied. Since the bridge sites are the most favorable adsorption sites and the migration of the O atom is from one bridge site to the neighboring bridge site on germanene surface, the corresponding state of the O atom adsorbed on the bridge site (site 1) can be regarded as initial state or final state in the CINEB method. In contrast, the states corresponding to the top sites (site 2 and site 3) can be regarded as different transition states because site 2 is not equivalent to site 3 in the low-buckled structure. Thus, there are two migration pathways considered in our calculations, which are denoted by "1-2-1" and "1-3-1", respectively, as shown in Fig. 5(a) and (b). The numbers represent the adsorption sites of O atom given in Fig. 4. The corresponding energy profiles along the optimized migration pathways are shown in Fig. 5. The calculated energy barriers are 1.43 eV and 1.28 eV for the two pathways,

which are higher than that of the migration of the O atom on silicene (1.18 eV and 1.05 eV),¹⁷ indicating that the mobility of the O atom on germanene is lower than that on silicene. In addition, similar to the migration of the O atom on silicene, the O atom moves along the edge of the string from the bridge site to the top site and then to the neighboring bridge site. However, it is worth noting that the migration pathway denoted by "1-2-1" is different from another migration pathway denoted by "1-3-1". Due to the adsorption of O atom on site 2 leading O atom to drop down to the basin plane of germanene after relaxation, O atom moves from bridge site 1 with higher position to top site 2 with lower position then to bridge site 1 with higher position. It can explain the difference of diagrammatic sketch between two migration pathways.

Furthermore, although the calculated results are obtained under ground state (0K), but even at room temperature (300K) the energy barrier of about 1.3 eV is not easy to overcome, indicating that the desorption of the adsorbed O atoms on germanene is relatively difficult. Therefore, although free-standing germanene is more stable than silicene in oxygen, but once oxygen molecule dissociates on germanene, the O₂-dissociation-induced O atoms adsorption prefers to form the germanium oxides.

IV. CONCLUSION

In conclusion, the O₂ dissociation and O atoms adsorption on germanene are studied by first-principles calcula-

tions in this letter. Compared with the spontaneous dissociation reaction of O₂ on silicene in oxygen, it is found that germanene is more stable than silicene because oxygen molecule can not easily dissociate into two O atoms, with overcoming the energy barrier of about 0.55 eV. On the other hand, oxygen molecule can be adsorbed on germanene surface with chemical adsorption, although the adsorption reaction is spontaneous. Moreover, O atom adsorption on germanene is rather different from the case on silicene, leading to two opposite migration pathways of O atom on germanene surface. Furthermore, once the oxygen molecule dissociates into two O atoms on germanene surface, the migration and desorption of O atoms are relatively difficult under room temperature due to the strong Ge-O bonds in the O-adsorbed germanene, which is in favor of forming germanium oxides in oxygen. The results provide compelling evidence to show that free-standing germanene is relatively stable in oxygen, which is different to silicene substantially. The work is helpful to reveal the detail of the interaction between oxygen molecule and free-standing germanene surface, and thus helpful to understand the stability of germanene in oxygen.

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- ¹ K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **306**, 666 (2004).
 - ² K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **438**, 197 (2005).
 - ³ A. K. Geim, *Science* **324**, 1530 (2009).
 - ⁴ R. Yan, Q. Zhang, Oleg A. Kirillov, W. Li, J. Basham, A. Boosalis, X. L. Liang, D. Jena, C. A. Richter, A. C. Seabaugh, D. J. Gundlach, H. G. Xing, and N. V. Nguyen, *Appl. Phys. Lett.* **102**, 123106 (2013).
 - ⁵ Y. J. Park, S. K. Lee, M. S. Kim, Hyunmin Kim and J. H. Ahn, *ACS Nano* **8**, 7655 (2014).
 - ⁶ S. Cahangirov, M. Topsakal, E. Aktürk, H. Sahin and S. Ciraci, *Phys. Rev. Lett.* **102**, 236804 (2009).
 - ⁷ L. Seixas, J. E. Padilha, and A. Fazzio, *Phys. Rev. B* **89**, 195403 (2014).
 - ⁸ Y. Ding, J. Ni, *Appl. Phys. Lett.* **95**, 083115 (2009).
 - ⁹ T. Y. Du, J. Zhao, G. Liu, J. X. Le, and B. Xu, *Modern Phys. Lett. B* **28**, 17 (2014).
 - ¹⁰ Nathanael J. Roome and J. David Carey, *ACS Appl. Mater. Interfaces* **6**, 7743 (2014).
 - ¹¹ C. C. Liu, W. X. Feng and Y. G. Yao, *Phys. Rev. Lett.* **107**, 076802 (2011).
 - ¹² P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. Le Lay, *Phys. Rev. Lett.* **108**, 15550 (2012).
 - ¹³ A. Fleurence, R. Friedlein, T. Osaki, H. Kawai, Y. Wang and Y. Yamada-Takamura *Phys. Rev. Lett.* **108**, 245501 (2012).
 - ¹⁴ L. Meng, Y. L. Wang, L. Z. Zhang, S. X. Du, R. T. Wu, L. F. Li, Y. Zhang, G. Li, H. T. Zhou, Werner A. Hofer and H. J. Gao, *Nanoletters* **13**, 685 (2013).
 - ¹⁵ E. Bianco, S. Butler, S. S. Jiang, O. D. Restrepo, W. Windl, and J. E. Goldberger, *ACS Nano* **7**, 4414 (2013).
 - ¹⁶ M. E. Dvila, L. Xian, S. Cahangirov, A. Rubio and G. Le Lay, *New Journal of Physics* **16**, 095002 (2014).
 - ¹⁷ G. Liu, X. L. Lei, M. S. Wu, B. Xu and C. Y. Ouyang, *EuroPhys. Lett.* **106**, 47001 (2014).
 - ¹⁸ A. Molle, C. Grazianetti, D. Chiappe, E. Cinquanta, E. Ciani, G. Tallarida and M. Fanciulli, *Adv. Funct. Mater.* **23**, 4340 (2013).
 - ¹⁹ G. Kresse, J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
 - ²⁰ G. Kresse, D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
 - ²¹ J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1991).
 - ²² H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
 - ²³ G. Henkelman, H. J. Jonsson, *Chem. Phys.* **113**, 9978 (2000).

TABLE I: Calculated adsorption energy E_{ad} and adsorption distance D for the adsorption of an O atom on different sites of germanene.

Sites	1(bridge)	2(top1)	3(top2)	4(center)
$D(\text{\AA})$	1.59	0.36	2.11	1.66
$E_{ad}(\text{eV})$	2.14	0.84	0.69	2.13

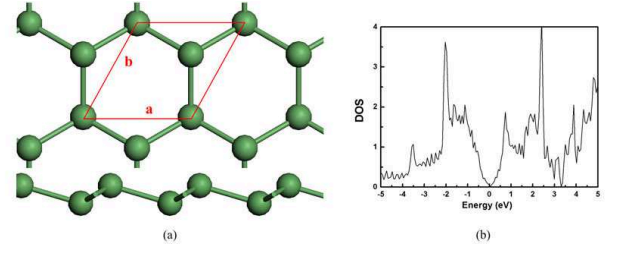


FIG. 1: (Color online) (a) Diagrammatic sketch of top and side views of germanene, (b) The DOS of unit germanene.

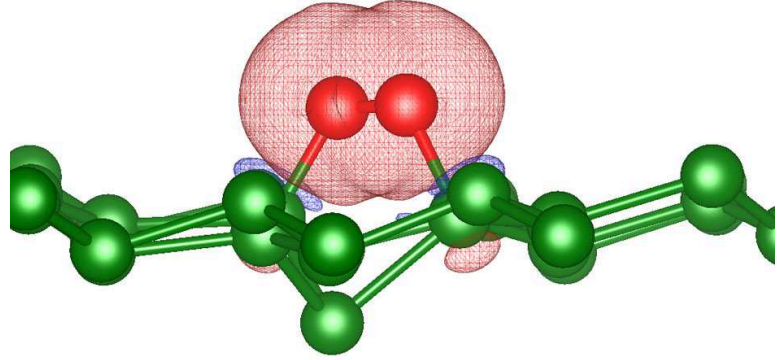


FIG. 2: (Color online) Isosurfaces of the induced charge density $\Delta\rho$ of the germanene adsorbed with an O_2 molecule. The green and red spheres are Ge and O atoms, respectively. The positive and negative isosurfaces are in redness and blue, respectively.

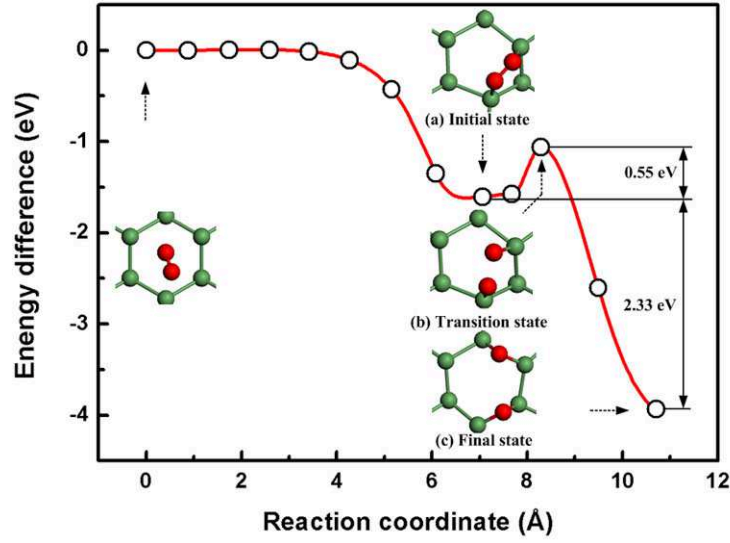


FIG. 3: (Color online) The optimized dissociation pathway of oxygen molecule on germanene

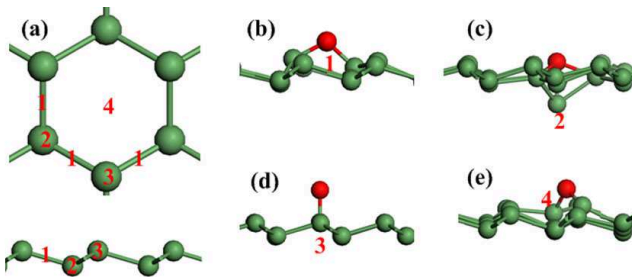


FIG. 4: (Color online) (a) Diagrammatic sketch of different adsorption sites of O atom on germanene surface, (b)-(d) represent optimized adsorption of O atom on bridge site, two different top sites and center site, respectively.

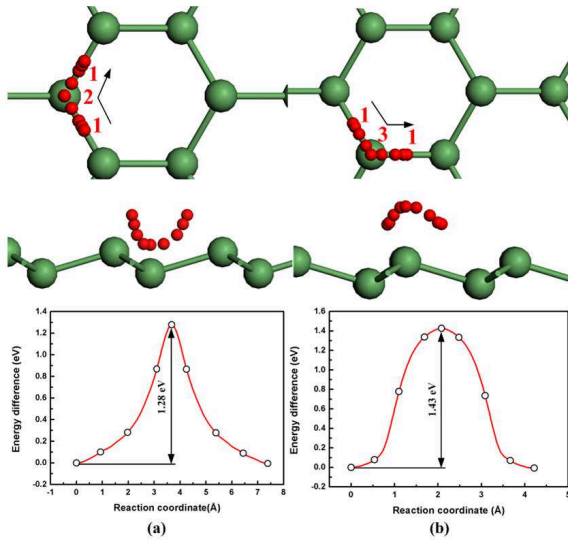


FIG. 5: (Color online) (a) Top and side views of the optimized migration pathway of an O atom migration along the pathway from site No. 1 to site No. 2 then to site No. 1 and its energy profile along the pathway on the germanene surface. (b) Top and side views of the optimized migration pathway of an O atom migration along the pathway from site No. 1 to site No. 3 then to site No. 1 and its energy profile along the pathway on the germanene surface. (Red color and green color represent O atoms and Ge atoms, respectively)